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Thermodynamic Analysis on Hydrogenation Process of Phenol of Bio-oil Model Compound

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Abstract. In this paper, the thermodynamics on the hydrogenation of phenol as a model compound of bio-oil was simulated based on Gibbs free energy minimization. The reaction system was determined according to the reaction mechanism of the phenol hydrogenation and the effects of reaction conditions on the equilibrium products were studied. The results show that benzene and cyclohexane are easily formed thermodynamically under reaction conditions. For the reaction system of selective hydrogenation of phenol to cyclohexanol, low temperature, high pressure and high molar ratio of hydrogen to phenol can improve the conversion of phenol and the selectivity of cyclohexanol. The optimum thermodynamic conditions for the hydrogenation of phenol to cyclohexanol are as follows: reaction temperature 400-600 K, reaction pressure 3.0-7.0 MPa, molar ratio of hydrogen to phenol 4.0-7.0. The simulation results are compared with the related experimental results.

1. Introduction

Bio-oil is a renewable energy which can be converted into liquid fuel. However, bio-pyrolysis oil with high oxygen content cannot be used directly as ordinary fuel, and must be treated by deoxidation and upgrading. Phenol has a relatively high content in bio-cracking oil. Catalytic hydrogenation of phenol to cyclohexanone and cyclohexanol has the advantages of simple method and environmental friendliness. Cyclohexanone and cyclohexanol are important raw materials and fine chemical intermediates.

In recent years, phenol hydrogenation catalysts have been studied extensively [1,2]. However, there are few studies on the thermodynamics of phenol hydrogenation. Resende et al [3] studied the thermodynamics of phenol gas phase hydrogenation and deoxidation reaction system in the temperature range 473-673 K, atmospheric pressure and hydrogen-phenol ratio in the range of 1-60. The effects of temperature on the equilibrium reaction system were analyzed for various reaction systems, and the influence of the molar ratio of hydrogen to phenol has also been discussed, but the effect of pressure change has not been discussed.

In order to fully explore the effects of reaction temperature, pressure and raw material ratio on the reaction, the thermodynamics of phenol hydrogenation was analyzed by the Gibbs reactor model in Aspen plus software. This study can provide reference for the process optimization and experimental catalyst improvement in industry.

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2. Calculation principles and methods

2.1. Reaction mechanism analysis

The products in phenol hydrodeoxygenation are complex and the different types of catalysts have different product selectivity [1,3]. According to the literature reports on phenol hydrogenation [4,5], a reaction path network is shown in Figure 1 and the reactions are summarized in Table 1.

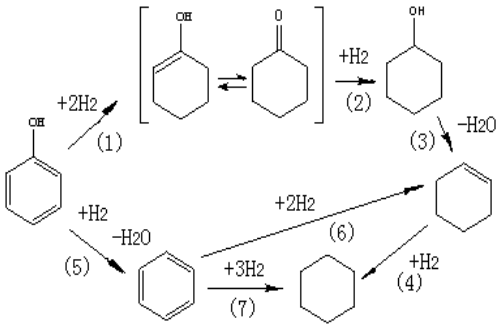


Figure 1. Pathways of phenol hydrogenation.

Table 1. Reactions in phenol hydrogenation

Reaction Equation	Main product and given code	No.
$C_6H_5OH+2H_2 \rightarrow C_6H_{10}O$	1-hydroxycyclohexene (1-hydroxy-C)	(1a)
$C_6H_5OH+2H_2 \rightarrow C_6H_{10}O$	Cyclohexanone (C-one)	(1b)
$C_6H_{10}O+H_2 \rightarrow C_6H_{12}O$	Cyclohexanol (C-ol)	(2)
$C_6H_{12}O \rightarrow C_6H_{10}+H_2O$	Cyclohexene (C_6H_{10})	(3)
$C_6H_{10}+H_2 \rightarrow C_6H_{12}$	Cyclohexane (C_6H_{12})	(4)
$C_6H_5OH+H_2 \rightarrow C_6H_6+ H_2O$	Benzene (C_6H_6)	(5)
$C_6H_6+2H_2 \rightarrow C_6H_{10}$	Cyclohexene(C_6H_{10})	(6)
$C_6H_6+3H_2 \rightarrow C_6H_{12}$	Cyclohexane (C_6H_{12})	(7)

Figure 1 and Table 1 show that there are two pathways for phenol hydrogenation. One is the hydrogenation of phenol to 1-hydroxycyclohexene (R1a) or cyclohexanone (R1b) and hydrogenation of cyclohexanone to cyclohexanol (R2), then cyclohexanol is dehydrated to cyclohexene (R3), and finally cyclohexene is hydrogenated to cyclohexane (R4). The second pathway is the direct hydrogenation of phenol to benzene (R5), which is then further hydrogenated to cyclohexene (R6) and cyclohexane (R7) .

2.2. Simulation method and parameters

According to the reaction path of phenol hydrogenation, the reaction system for phenol hydrogenation analysis was determined.

(1) The first reaction system of phenol hydrogenation (denoted by RSI): Reaction system was determined by the reactions of (R1-R7). The reaction substance system consisted of phenol, H_2, 1-hydroxycyclohexene, cyclohexanone, cyclohexanol, cyclohexene, cyclohexane, benzene and H_2O.

According to the different selectivity of catalyst, a simple reaction mechanism diagram for the hydrogenation of phenol to cyclohexanone and cyclohexanol was obtained [6]. In order to analyze the thermodynamic law of selective hydrogenation of phenol to cyclohexanol, a simplified reaction system of phenol hydrogenation was also discussed.

(2) The second reaction system of phenol hydrogenation (denoted by RSII): The reaction system determined by the reactions of (R1-R2) was considered and cyclohexanol was the target product. The reaction system includes phenol, H_2, 1-hydroxycyclohexene, cyclohexanone, cyclohexanol and H_2O.

The thermodynamic law of phenol hydrogenation was analyzed by Gibbs free energy minimization method. The parameters used in thermodynamic analysis are conversion of phenol/H_2 and selectivity of products, which are defined as follows:

$$X(i) = [(F_{i,in} - F_{i,out}) / F_{i,in}] \times 100\% \quad (1)$$

$$S(jc) = [F_{jc,out} / (F_{phenol,in} - F_{phenol,out})] \times 100\% \quad (2)$$

In which, $X(i)$ is the conversion of the raw material i, %; F is the molar flow rate of substance, kmol/hr; $S(jc)$ is the selectivity of carbon-containing substances, %; Subscript i denotes the raw material of phenol or hydrogen; Subscripts *in* and *out* indicate the state of pre-reaction and balanced output respectively; Subscript jc is a component of carbon products $C_6H_{10}O$ (C-one), $C_6H_{10}O$ (1-hydroxy-C), $C_6H_{12}O$ (C-ol), C_6H_{10}, C_6H_{12} and C_6H_6.

3. Results and discussion

3.1. Effect of reaction temperature on the equilibrium constants of each reaction

Based on the thermodynamic equation and the thermodynamic data of the corresponding substances, the thermodynamic parameters of the phenol hydrogenation system in the temperature range of 298-998 K were calculated. The equilibrium constants of the reactions varies with the temperature as shown in Figure 2.

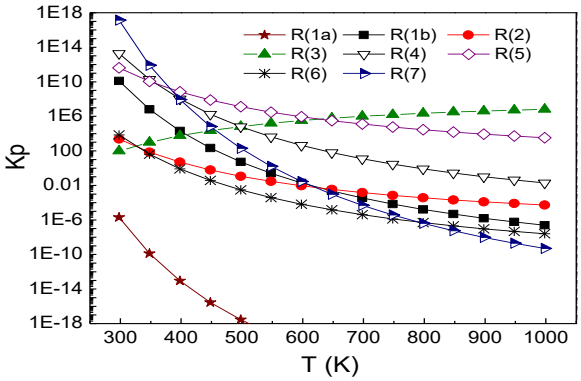


Figure 2. Effect of reaction temperature on the equilibrium constants of each reaction

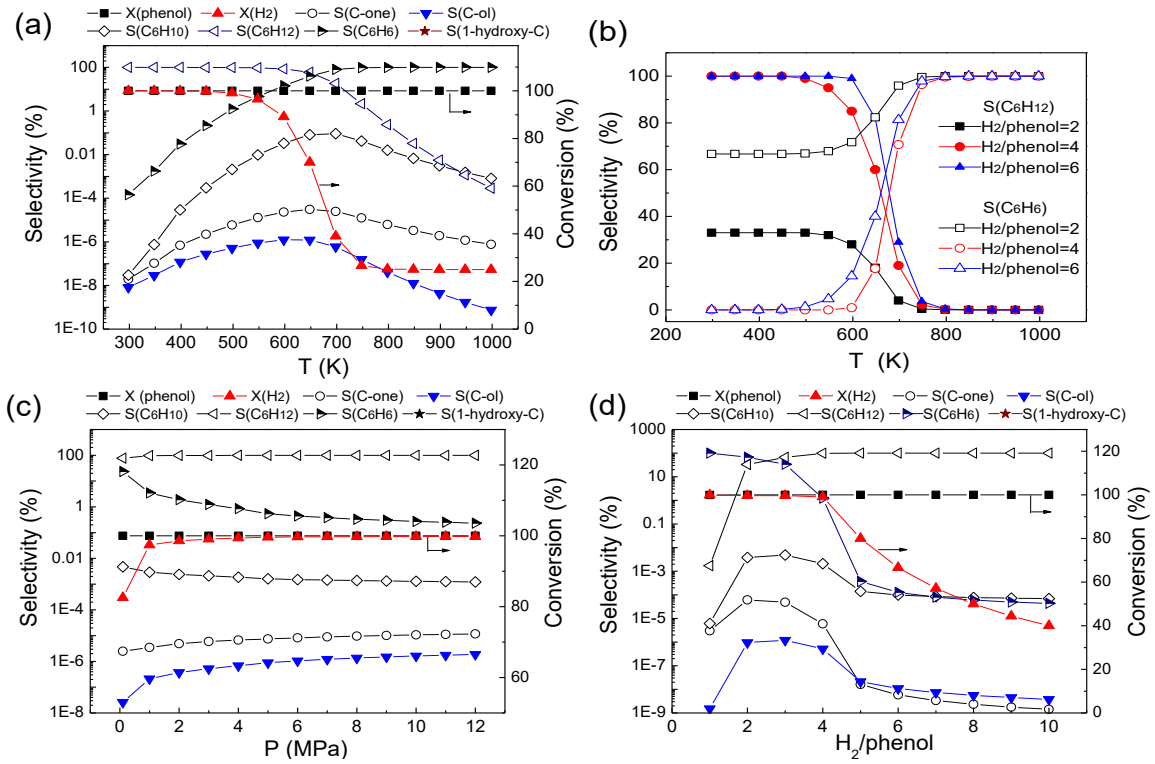
Thermodynamic results show that the enthalpy of each reaction in the hydrogenation of phenol varies little with temperature, while the Gibbs free energy of each equation varies with temperature in varying degrees. Figure 2 shows that the reaction temperature has a great influence on the equilibrium constants of each reaction, and the equilibrium constants of each reaction are quite different. The equilibrium constant for the formation of 1-hydroxycyclohexene is much lower than that for the reaction of other substances, indicating that 1-hydroxycyclohexene is an intermediate substance. The reaction equilibrium constant of cyclohexane formation (R7) is high at low temperature. The equilibrium constants for the formation of cyclohexene (R3), cyclohexane (R4) from hydrogenated cyclohexene and benzene (R5) are high in high temperature range. At 548 K, the equilibrium constant K_p of the reaction (R1b) for cyclohexanone formation was only 0.25, while K_p of benzene formation (R5) reached 10^6. The equilibrium constant for the formation of cyclohexanol (R2) are 2×10^3 at 298 K and 0.03 at 548 K, indicating that high temperature is not conducive to the reaction (R2) .

3.2. Effects of reaction conditions on the first reaction system (RSI)

For the first reaction system (RSI), the effects of temperature, pressure and the molar ratio of hydrogen to phenol on the conversion of phenol and the selectivity of the products are shown in Figure 3 under the reaction conditions of 298-998 K, 0.1-12.0 MPa and 1.0-10.0 molar ratio of H_2/phenol.

As seen in Figure 3(a,c,d), the conversion of phenol is very high under the reaction conditions, which is nearly 100%. The selectivities of cyclohexane and benzene are all very high in the products, and the selectivities of other substances are very low. The selectivity of 1-hydroxycyclohexene is below -10^{24}, which is not shown in figure. This result is consistent with the analysis of equilibrium constants. Figure 3(b) shows that the selectivity of benzene increases with the increase of reaction temperature, while the selectivity of cyclohexane decreases, mainly because the equilibrium constant of cyclohexane formation decreases greatly with the increase of reaction temperature than that of benzene formation. This is consistent with the relevant research conclusions [3].

Figure 3(c) shows that the pressure has little effect on the selectivity of the reaction products. In the low pressure range, the selectivity of cyclohexane increases and benzene decreases with the increase of pressure. When the pressure is up to 5.0 MPa, the selectivity of other products except cyclohexane is very low. Figure 3(d) shows that with the increase of the molar ratio of hydrogen to phenol, the selectivity of cyclohexane increases gradually, the selectivity of benzene decreases gradually, while the selectivity of other products increases first and then decreases.



. Figure 3. Effects of reaction conditions on the first reaction system (RSI) of phenol hydrogenation. Reaction conditions: (a) H_2/phenol=4.0, 3.0 MPa; (b) 3.0 MPa; (c) H_2/phenol=4.0, 498 K; (d) 3.0 MPa, 498 K.

3.3. Effects of reaction conditions on the second reaction system (RSII)

3.3.1. Effects of reaction temperature. The effects of reaction temperature on the second reaction system (RSII) are shown in Figure 4.

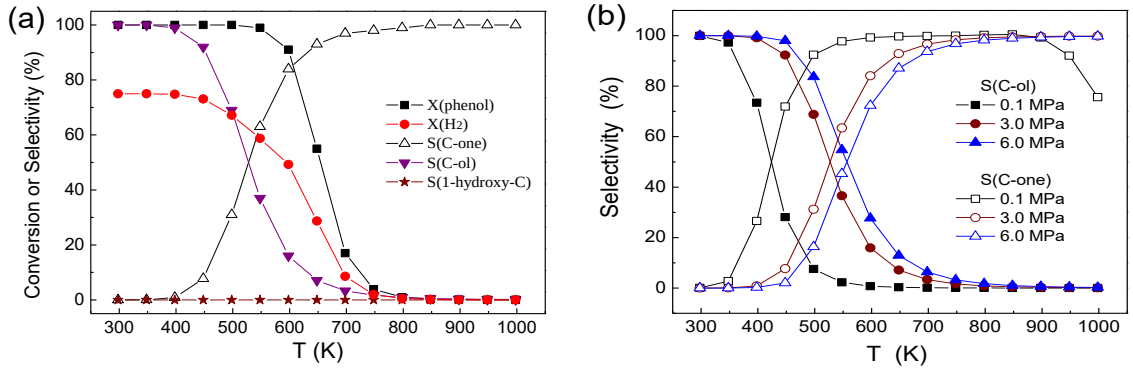


Figure 4. Effects of reaction temperature on the second reaction system (RSII) of phenol hydrogenation. Reaction conditions: (a) 3.0 MPa, H_2/phenol = 4.0; (b) H_2/phenol = 4.0.

Figure 4(a) shows that reaction temperature has a great influence on the equilibrium products of phenol hydrogenation. With the increase of temperature, the conversions of phenol and hydrogen decrease gradually, the selectivity of cyclohexanone increases, the selectivity of cyclohexanol decreases, and the selectivity of 1-hydroxycyclohexene is zero. The temperature range of conversion of raw materials and selectivity of products varied greatly from 500 K to 700 K. Figure 4(b) shows that the selectivity of cyclohexanone increases with the increase of reaction temperature and the

decrease of pressure. The selectivity of cyclohexanol is contrary to that of cyclohexanone. Therefore, the hydrogenation of phenol to cyclohexanol should be carried out at a lower reaction temperature.

3.3.2. Effects of reaction pressure and molar ratio of raw materials. The effects of reaction pressure and hydrogen-phenol molar ratio on on the second reaction system (RSII) are shown in Figure 5.

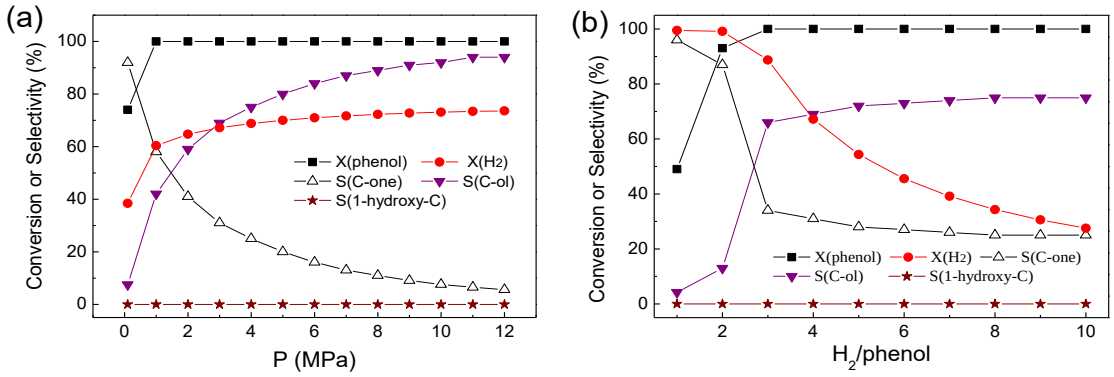


Figure 5. Effects of pressure and H_2/phenol on the second reaction system (RSII) of phenol hydrogenation. Reaction conditions: (a) 498 K, H_2/phenol= 4.0; (b) 498 K, 3.0 MPa.

From Figure 5(a, b), when the pressure is greater than 0.1 MPa and the molar ratio of H_2/phenol is greater than 3.0, the conversion of phenol is close to 100%. The conversion of hydrogen increases with the increase of pressure and the decrease of molar ratio of H_2/phenol. With the increase of pressure and the molar ratio of H_2/phenol, the selectivity of cyclohexanone decreases and the selectivity of cyclohexanol increases. The selectivity of 1-hydroxycyclohexene is close to zero, indicating that 1-hydroxycyclohexene is an intermediate product. Increasing the reaction pressure is helpful to improve the conversion of phenol and the selectivity of cyclohexanol [7], but if the pressure is too high, the equipment cost will be increased. Therefore, the appropriate reaction pressure for phenol hydrogenation to cyclohexanol is 3.0-7.0 MPa. Increasing H_2/phenol is conducive to improving the conversion of phenol and the selectivity of cyclohexanol, but excessive hydrogen will cause waste and increase the cost. Therefore, the appropriate H_2/phenol molar ratio for the hydrogenation of phenol to cyclohexanol is 4.0-7.0.

3.4. Comparisons between calculated and experimental results

The thermodynamic calculation is compared with the related experimental results, as shown in Table 2.

Table 2. Comparison of this calculation result with related experimental results.

Catalyst /Analysis method	Reaction conditions	*X* (phenol)	Selectivity		References
			S (C-ol)	*S* (C-one)	
Pd /CNTs	423 K, 2.2 MPa, H_2/phenol=4.0	43.2%	25.2%	68.4%	[2]
Ni-B/γ-Al_2O_3	393 K, 3.0 MPa	49.0%	95.5%	4.5%	[7]
1% Pd/MgO	503 K, WHSV=0.027mol $h^{-1}g^{-1}$, H_2/phenol=4.0	90%	-	100%	[8]
6% Pd/C	453K, H_2/phenol=4.0	50%	-	100%	[9]
Co_3O_4/ CN	433 K, 3.0 MPa	98%	-	80%	[10]
Gibbs free energy minimization	RSII: 448 K, 3.0 MPa, H_2/phenol=4.0 548 K, 3.0 MPa, H_2/phenol=4.0	100 % 99.4%	92.3 % 36.5 %	7.7 % 63.5 %	This study

Table 2 shows that the main product of phenol hydrogenation on some catalysts is cyclohexanol under reaction conditions [7], while the main product of hydrogenation on others is cyclohexanone [2,8-10]. According to thermodynamic analysis, the selectivities of cyclohexanol and cyclohexanone are closely related to the reaction temperature. Table 2 shows that the calculated results are in good agreement with the experimental results. The conversion of phenol on some catalysts is relatively low, which indicates that the hydrogenation catalysts need further improvement.

4. Conclusions

Based on two different phenol hydrogenation mechanisms, the thermodynamic calculation of phenol hydrogenation was carried out by Gibbs free energy minimization method. The effects of temperature, pressure and molar ratio of hydrogen to phenol on the equilibrium product composition were analyzed. The comparison results also show that the calculated results in this paper are consistent with the experimental results. The conclusions of this study are as follows:

(1) For the first reaction system of phenol hydrogenation (RSI), under the reaction conditions, the conversion of phenol is always close to 100%. Cyclohexane and benzene are the main products, cyclohexane has high selectivity at low temperature, benzene has high selectivity at high temperature, and other products have low selectivity.

(2) For the second reaction system of phenol hydrogenation (RSII), low temperature, high pressure and high H_2/phenol molar ratio are beneficial to improve the conversion of phenol and the selectivity of cyclohexanol in the product. The optimum thermodynamic conditions for hydrogenation of phenol to cyclohexanol are as follows: reaction temperature is 400-600 K, reaction pressure is 3.0-7.0 MPa, and the molar ratio of hydrogen to phenol is 4.0-7.0.

Acknowledgements

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